METHOD 15A

STANDARDIZATION AND ANALYSIS OF PERMANENT GASES AND METHANE

Ref: Reg. 2-1-307
8-34-111.2, 114, 301

1. PRINCIPLE

1.1 Standard gases used for calibrating source test instruments must be checked periodically for accuracy and quality assurance purposes.

1.2 This method is applicable to the determination of permanent gases such as carbon monoxide, carbon dioxide, oxygen and nitrogen and methane, in % concentration, in samples collected from municipal landfills and other sources.

1.3 An aliquot of the sample is injected into a gas chromatograph, fitted with a thermal conductivity detector and a data station, to determine the concentrations of methane and permanent gases.

1.4 The method has a detection limit of 80 ppm for carbon monoxide (CO), 200 ppm for carbon dioxide (CO_2), 0.5% for oxygen (O_2), 0.5% for nitrogen (N_2) and 0.1% for methane (CH_4).

1.5 Interference:

1.5.1 A big nitrogen peak can mask a small oxygen peak and if this happens, the area under the oxygen peak will not be integrated properly. The concentration of oxygen must be calculated using peak height instead of peak area.

2. APPARATUS

2.1 Gas Chromatograph. This unit is fitted with a gas sampling valve, a sample loop, a thermal conductivity detector, a temperature programmer and a compatible integrator or data station. The GC operating parameters are:

Initial Oven Temp.	35^{o} C
Initial Hold Time	10 min.
Temp. Program Rate	20^{o} C/min.
Final Oven Temp.	165^{o} C
Final Hold Time	30 min.
Detector Temp.	170^{o} C
Filament Current	240 ma (medium)
Carrier Gas	He

Carrier Gas Flow	20 ml/min.
TCD Polarity	A-B or B-A
Sample Loop Size	0.5 - 5.0

2.2 Analytical Column: Any analytical column capable of resolving carbon dioxide, carbon monoxide, oxygen, nitrogen and methane from each other is acceptable. The recommended column for this method is:

2.2.1 20' x 1/8" O.D. SS packed with Carbosieve II, 80/100 mesh.

2.3 Gas Tight Syringe. 30 ml capacity.

2.4 Two Stage Regulator, with a controlling valve.

3. REAGENTS

3.1 Cylinder Helium.

3.2 NIST Traceable Calibration Standards. These standards can be purchased from a specialty gas company.

4. ANALYTICAL PROCEDURE

4.1 Set up the gas chromatograph as described in Section 2.1.

4.2 Using a clean dry 30 ml gas tight syringe, inject 10 to 15 ml room air into the GC through the sampling valve. Repeat this procedure until the baseline is stabilized.

4.3 Once the baseline is stabilized, repeat (4.2), this time injecting the standard gases. Record the retention times and the peak areas of the compounds of interest. Retain the chromatogram.

4.4 Repeat (4.3), this time injecting the sample. Record the retention times and peak areas of the analytes. Retain the chromatogram.

4.5 All injections must be in duplicate and the area counts must not differ by more than (+/-) 2 - 5% of the average area counts.

5. CALCULATION

5.1 Compare the chromatogram obtained with the standard compounds (4.3) to that of the analytes (4.4) to confirm the identities of the compounds of interest. Quantitate the concentration of each analyte in the sample using the following equation: (NOTE 1).

5.1.1 $\text{Conc.}_{(Sam)} = \frac{PA_{(Sam)} \times \text{Conc.}_{(Std)}}{} \times DF$ (NOTE 1)

$PA_{(Std)}$

Where:

$Conc._{(Sam)}$ = Concentration of the analyte in ppm or %(v/v)

$Conc._{(Std)}$ = Concentration of the Standard in ppm or %(v/v)

$PA_{(Sam)}$ = Peak area of the analyte

$PA_{(Std)}$ = Peak Area of the Standard

NOTE 1: Peak Height (PH) may be substituted for Peak Area (PA) in (5.1.1).

5.1.2 For the standardization of calibration gases, calculate also the % bias using the following equation:

$$\% \text{ Bias} = \frac{\text{Assigned Conc. - Analyzed Conc.}}{\text{Assigned Conc.}} \times 100$$

7. REFERENCE

7.1 EPA Method 3C - Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Source. CFR Vol. 56, No. 104 p 24522, May 30, 1991.